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| (21) International Application Number: PCT/GB91/00450 (22) International Filing Date: 26 March 1991 (26.03.91) (30) Priority data: 9006737.2 26 March 1990 (26.03.90) GB (71) Applicant (for all designated States except US): COUR- TAULDS COATINGS (HOLDINGS) LIMITED [GB/ GB]; 18 Hanover Square, London W1A 1AD (GB). (72) Inventors; and (75) Inventors/Applicants (for US only) : O'KEEFFE, Luke, James [GB/GB]; 183 Wingrove Road, Fenham, Newcas- tle upon Tyne NE4 9DA (GB). NIXON, Steven, Alistair [GB/GB]; 17 Glenwood Walk, Chapel Park, Newcastle upon Tyne NE5 1ST (GB). CAMERON, Colin [GB/ GB]; 140 Normount Road, Newcastle upon Tyne NE4 8SJ (GB). PENMAN, Alan, Keith [GB/GB]; 8 Friarside Crescent, Rowlands Gill, Tyne & Wear NE39 1DQ (GB). | | (74) Agents: SENIOR, Janet et al.; Abel & Imray, Northum- berland House, 303-306 High Holborn, London WC1V 7LH (GB). (81) Designated States: AT (European patent), AU, BE (Euro- pean patent), BR, CA, CH (European patent), DE (Eu- ropean patent), DK (European patent), ES (European patent), FI, FR (European patent), GB (European pa- tent), GR (European patent), HU, IT (European patent), JP, KR, LU (European patent), NL (European patent), NO, PL, SE (European patent), SU, US. Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i> |

(4) Title: COATING COMPOSITIONS

(57) Abstract

A thermosetting powder coating composition according to the present invention comprises as binder a co-reactable particulate mixture of a carboxylic acid-functional polyester component and a curing agent having groups reactive with carboxylic acid groups, characterized in that the carboxylic acid-functional component comprises a semi-crystalline polyester having an acid value of from 10 to 70 mg KOH/g and a hydroxy value of no more than 11 mg KOH/g. Generally the semi-crystalline polyester has one or more Tg values less than 55 °C, a sharp melting point of 50 to 200 °C and preferably a number average molecular weight of at least 1600. The composition may, if desired, include an amorphous polyester and the curing agent may be, for example, an epoxy resin or a bis(beta-hydroxyalkylamide). Coating compositions of the invention cure faster than in the absence of semi-crystalline polyesters and the thermoset coatings prepared therefrom have improved appearance and mechanical properties (especially flexibility).

CLAIMS

1. A thermosetting powder coating composition comprising as binder a co-reactable particulate mixture of a carboxylic acid-functional polyester component and a curing agent having groups reactive with carboxylic acid groups, characterised in that the carboxylic acid-functional component comprises:

(A) 5-100% by weight of at least one semi-crystalline polyester having an acid value of from 10 to 70 mg KOH per gram and a hydroxy value of no more than 11 mg KOH per gram; and

(B) 0-95% by weight of at least one amorphous polyester having a T_g of at least 30°C and an acid number of 15 to 90.

2. A composition according to claim 1, characterised in that the binder comprises 40-98% by weight of the carboxylic acid-functional polyester component and 2-60% by weight of the curing agent.

3. A composition according to claim 1 or 2, characterised in that the semi-crystalline polyester has a number average molecular weight of 1600 to 12,000.

4. A composition according to claim 3, characterised in that the semi-crystalline polyester has a number average molecular weight of 2500 to 4500.

5. A composition according to any of claims 1 to 4, characterised in that the semi-crystalline polyester has an acid value of 28 to 45.

6. A composition according to any of claims 1 to 5, characterised in that the semi-crystalline polyester has a hydroxy value of no more than 5.

7. A composition according to any of claims 1 to 6, characterised in that the semi-crystalline polyester has a melt viscosity of from 0.1 to 7 Pa s (1 to 70 pise) at 200°C and from 4 to 20 Pa s (40 to 200 pois) at 160°C.

5 8. A composition according to any of claims 1 to 7, characterised in that the carboxylic acid-functional polyester component comprises 5 to 90% by weight of semi-crystalline polyester (A) and 10-95% by weight of amorphous polyester (B).

10 9. A composition according to claim 8, characterised in that the carboxylic acid-functional polyester component comprises 10-40% by weight of semi-crystalline polyester (A) and 60-90% by weight of amorphous polyester (B).

15 10. A composition according to claim 8 or claim 9, in which the amorphous polyester is based on a condensation reaction of a polyol component comprising one or more aliphatic or cycloaliphatic polyols with an acid component comprising one or more aliphatic, cycloaliphatic or aromatic polycarboxylic acids or an anhydride, ester or acid chloride thereof, characterised in that at least 10% by weight of the acid component is isophthalic acid.

20 11. A composition according to claim 10, characterised in that at least 40% by weight of the acid component is isophthalic acid.

25 12. A composition according to any of claims 1 to 11, characterised in that the curing agent is a polyepoxide and the molar ratio of epoxide groups in the curing agent to carboxylic acid groups in the polyester component is 0.6 to 1.6:1.

30 13. A composition according to claim 12, characterised in that the polyepoxid is an epoxy resin of epoxide equivalent weight 150-1000 and the weight ratio of

epoxy resin to polyester component is 15:85 to 60:40.

14. A composition according to claim 12, characterised in that the curing agent is a solid non-resinous polyepoxide.

5 15. A composition according to any of claims 1 to 11, characterised in that the curing agent is a bis(beta-hydroxyalkylamide).

10 16. A semi-crystalline polyester for use in thermosetting powder coatings with one or more Tg values less than 55°C, a sharp melting point of 50°C to 200°C, an acid value of from 10 to 70 mg KOH per gram and a hydroxy number of no more than 11 mg KOH per gram.

15 17. A semi-crystalline polyester according to claim 16, characterised in that it has a number average molecular weight of at least 1600.

18. A semi-crystalline polyester according to claim 16 or claim 17, characterised in that it has a number average molecular weight of up to 12,000.

20 19. A semi-crystalline polyester according to claim 18, characterised in that it has a number average molecular weight of 2500 to 4500.

20. A semi-crystalline polyester according to any of claims 16 to 19, characterised in that it has an acid value of 28 to 45.

25 21. A semi-crystalline polyester according to any of claims 16 to 20, characterised in that it has a hydroxy value of no more than 5.

22. A semi-crystalline polyester according to any of claims 16 to 21, characterised in that it has a melt

viscosity f from 0.1 to 7 Pa s (1 to 70 pois) at 200°C
and from 4 to 20 Pa s (40 to 200 pois) at 160°C.

23. A process for the preparation of a thermosetting powder coating composition, characterised in that a co-reactable particulate mixture of a carboxylic acid-functional polyester component as defined in claim 1, a curing agent and optionally one or more pigments and/or other additive(s) is blended and comminuted.

24. A process according to claim 23, characterised in that after melting in the blending step the semi-crystalline polyester is recrystallised by an annealing treatment.

25. A thermosetting powder coating composition prepared according to claim 23 or claim 24.

26. A process for the preparation of a semi-crystalline polyester for use in thermosetting powder coatings, by polycondensation between one or more suitable polyols and one or more suitable polycarboxylic acid components selected from acids, anhydrides, esters and acid halides, characterised in that excess of acid over alcohol is used to give a product having an acid value of from 10 to 70 mg KOH/g and a hydroxy value of no more than 11 mg KOH/g.

27. A semi-crystalline polyester prepared according to claim 26.

28. A process for coating a substrate characterised in that the thermosetting powder coating composition of any of claims 1 to 15 or claim 25 is applied to the substrate and is heated on the substrate to fuse and cure the coating.

29. A substrate when coated by a process according to claim 28.

INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 91/00450

I. CLASSIFICATION F SUBJECT MATTER (If several classification symbols apply, indicate all) *

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC⁵: C 09 D 167/00, C 08 G 63/18

II. FIELDS SEARCHED

Minimum Documentation Searched *

Classification System

Classification Symbols

IPC⁵

C 09 D, C 08 G

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched *

III. DOCUMENTS CONSIDERED TO BE RELEVANT *

| Category * | Citation of Document, ** with Indication, where appropriate, of the relevant passages ** | Relevant to Claim No. ** |
|------------|--|--------------------------|
| X | US, A, 4217426 (R.L. McCONNELL) 12th August 1980 see claims 1-8 cited in the application ----- | 16 |
| X | GB, A, 2189498 (U.C.B.) 28th October 1987 see claims 1-23 | 26, 27 |
| A | ----- | 1 |
| A | EP, A, 0322834 (PPG INDUSTRIES) 5th July 1989 see claims 1-5 ----- | 1, 2, 15 |
| A | CH, A, 614733 (INVENTA AG) 14th December 1979 see claims 1-3 ----- | 1 |
| | ./. | |

* Special categories of cited documents: **

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"Z" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

18th July 1991

Date of Mailing of this International Search Report

30. 08. 91

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

M. PEIS

M. Peis

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

| Category * | Citation of Document, " with indication, where appropriate, of the relevant passages | Relevant to Claim No. |
|------------|--|-----------------------|
| A | EP, A, 0010805 (UNILEVER NV) 14th May 1980 see claim 1; page 3, lines 19-23 | 1 |
| A | ----- EP, A, 0038635 (DAINIPPON INK AND CHEMICALS, INC.) 28th October 1981 see claims 1-10 | 1 |
| A | ----- WO, A, 89105320 (EASTMAN KODAK) 15th June 1989 see claim 1 cited in the application ----- | 1 |

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

GB 9100450
SA 46162

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 26/08/91. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|----------------------------|---------------------|
| US-A- 4217426 | 12-08-80 | US-A- 4155952 | 22-05-79 |
| GB-A- 2189498 | 28-10-87 | CA-A- 1273739 | 04-09-90 |
| | | US-A- 4740580 | 26-04-88 |
| EP-A- 0322834 | 05-07-89 | US-A- 4801680 | 31-01-89 |
| | | JP-A- 2003458 | 09-01-90 |
| CH-A- 614733 | 14-12-79 | None | |
| EP-A- 0010805 | 14-05-80 | NL-A- 7810813 | 02-05-80 |
| | | AT-T- 674 | 15-02-82 |
| | | BE-A- 879782 | 30-04-80 |
| | | US-A- 4340698 | 20-07-82 |
| EP-A- 0038635 | 28-10-81 | JP-A- 56136856 | 26-10-81 |
| | | US-A- 4499239 | 12-02-85 |
| WO-A-89105320 | | None | |